Strategies for chemically healthy public swimming pools

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DTU Environment
Department of Environmental Engineering

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Preface

This PhD thesis is based on work carried out at the Department of Environmental Engineering at the Technical University of Denmark in the period from January 2009 to February 2013. The project was supervised by Associate Professor Henrik R Andersen, Professor Hans-Jørgen Albrechtsen and Emeritus Professor Hans Mosbæk.

The thesis is based on four scientific papers, which are referred to with the roman numbers (e.g. **Paper I**).

I. Hansen, Kamilla M.S., Willach, Sarah, Antoniou, Maria G., Mosbæk, Hans, Albrechtsen, Hans-Jørgen and Andersen, Henrik R., 2012. Effect of pH on the formation of disinfection byproducts in swimming pool water – Is less THM better? *Water Research*, 46(19), 6399-6409.

II. Hansen, Kamilla M.S., Willach, Sarah, Mosbæk, Hans, Andersen, Henrik R., 2012. Particles in swimming pool filters – Does pH determine the DBP formation? *Chemosphere*, 87(3), 241-247.

III. Hansen, Kamilla M.S., Zortea, Raissa, Piketty, Aurelia, Vega, Sergio Rodriguez, Andersen, Henrik R., 2013. Photolytic removal of DBPs by medium pressure UV in swimming pool water. *Science of the Total Environment*, 443, 850-856.

IV. Hansen, Kamilla M.S., Albrectsen, Hans-Jørgen, Andersen, Henrik R., Optimal pH in chlorinated swimming pools – balancing formation of byproducts, Draft.

In this online version of the thesis, the articles are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from DTU Environment, Technical University of Denmark, Miljøvej, Building 113, 2800 Kgs. Lyngby, Denmark, reception@env.dtu.dk.

During the PhD study I presented the work at national and international meetings and conferences. Furthermore, I have worked on a national report. This has lead to the following 5 abstracts, conference article and report:

Hansen, K.M.S., Willach, S., Mosbæk, H., Albrechtsen, H.-J. and Andersen, H.R. Effect of selection of pH in swimming pools on formation of chlorination by-products. Fourth International Swimming Pool & Spa Conference, Research and Development on Health, Air and Water Quality Aspects of the Man-made Recreational Water Environment, March 15 – 18, 2011, Porto, Portugal. Conference article in proceeding and oral presentation.

Hansen, K.M.S., Andersen, H.R. Effekten af pH på dannelsen af biprodukter – Måler vi for de relevante biprodukter? Dansk Svømmebadsteknisk Forenings Årsmøde, April 13 – 14, 2011, Herning, Denmark. Oral presentation and abstract in Svømmebadet.

Hansen, K.M.S. Does pH determine the DBP formation? Pool's 12, First international workshop on swimming pool research. 3 – 4 May, 2012, Delft, Nederlands. Abstract and oral presentation.

Hansen, K.M.S. Photolytic removal of DBPs by medium pressure UV. Pool's 12, First international workshop on swimming pool research. 3 – 4 May, 2012, Delft, Nederlands. Abstract and oral presentation.

Hansen, K.M.S., and Andersen, H.R. Effekt af pH på dannelse af flygtige klorbiprodukter i svømmebade (Effect of pH on formation of volatile chloro-organinic byproducts) In Danish. Naturstyrelsen, 2012. ISBN: 978-87-7279-394-8

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Kamilla M.S. Hansen

Abstract

Swimming pools are used around the world for recreational, rehabilitation and physical activity and therefore it is imperative that the water and air quality are safe for the health of the bathers. Chlorination is by far the most widely applied method to control pool water quality and to prevent spreading of pathogens between swimmers because of its residual disinfection effect. In addition to potential contamination of pathogenic microorganisms, swimming pool water is polluted by organic matter deposited from the bathers such as saliva, urine, sweat, hair and personal care products. Since chlorine is a strong oxidant it oxidizes the organic matter in the pool water and forms disinfection byproducts (DBPs). More than 100 different DBPs have been identified. Some of these have been found to be genotoxic and may pose an increased cancer risk for the bathers.

The aim of this thesis was to give an overview of the strategies which can be used to achieve microbiological safe water with low levels of DBPs to ensure healthy environment for bathers.

There are different approaches to achieve healthy environment in public swimming pools which in this thesis are divided into three strategies: alternatives to chlorination, removal of precursors and DBPs, and inhibition of the DBP formation. None of the alternative disinfection agents which are used for private swimming pools are applicable for public swimming pools. Thus chlorine is the most likely future disinfectant in public swimming pools. The strategy with removal of precursors and DBPs includes several methods: pre-swim showering, filtration, ozonation, activated carbon, stripping, and UV treatment. In general, decreasing the load of precursors by requiring pre-swim showering would decrease the formation of DBPs. However, addition of precursors cannot be completely avoided. Hair and skin cells are precursors for DBPs so good filtration with fast removal of particles could also be an option to obtain lower DBPs formation. Another way to remove precursors is to ozonate the pool water, since ozonation of the precursors leads to organic compound which is less reactive towards chlorine. Ozone is also able to remove combined chlorine and other DBPs but the reaction is slow. Activated carbon is able to adsorb precursors and DBPs except chloramines which are removed by catalytic reaction. Formation of DBPs is unavoidable. However, the volatile DBPs can be removed by stripping while UV treatment is used for control of combined chlorine levels. The last strategy with inhibition of the DBP formation mainly focused on pH since change in temperature and chlorine level are very limited due to comfort and safety of the bathers.

The aim of the PhD study was to investigate the possibility of UV used for combined chlorine removal to remove other DBPs and to investigate the effect of pH on the formation of selected DBPs.

The investigations were carried out in laboratory setups in order to have controlled experimental conditions. The UV treatment can remove a range of DBPs but with varying efficiency. In general, the photolysis efficiency increased with bromine substitution of chlorine in the structure of the DBPs. Combined chlorine was used as actinometer to estimate the removal which could be expected at actual UV treatment applied in swimming pools if no other formation or removal pathways are considered. For very volatile DBPs, the removal by UV treatment will be relative low for the fate of the DBP unless it is very easily photolysed (such as trichloronitromethane). For non-volatile DBPs, the sensitivity for photolysis is important to achieve significant removal of the DBPs by UV treatment. The investigation suggested a significant removal of trichloronitromethane, chloral hydrate and the bromine containing haloacetonitriles and trihalomethanes may occur as a beneficial side-effect of chloramine control by UV in swimming pools.

Changing the pH value of the pool water affected the investigated groups of DBPs differently. An analogue consisting of the main component in urine and sweat and particles consisting of skin cells and hair were used as precursor material and in both cases the formation of THMs decreased with decreasing pH while HAN formation increased. The effect of pH on the formation of HAAs depended on the precursor type. The particles did not form trichloramine during chlorination whereas the body fluid analogue formed trichloramine. The trichloramine formation showed strong pH dependency with increasing formation at pH below 7.0. The presence of bromide did not change the impact of pH on the DBP formation, but it did increase the total amount of formed DBPs. The estimated toxicity increased with decreasing pH similar to the HAN formation. From evaluation of which DBPs were formed, theirs extent and theirs toxicity, an optimal pH range for pool waters was identified to pH 7.0 – 7.2. It is estimated that in the wider pH range (pH 6.8 – 7.5) the pH effect on DBP formation was minimal compared to other factors which may affect the formation of DBPs in swimming pools.

The future swimming pool will make use of several methods to minimise the level of DBPs in the pool. The different methods have to be optimised together to ensure the best water quality. The aim should not be only to minimise level of trihalomethanes since other and more toxic DBPs are formed and these does not always follow the same tendency as trihalomethanes (e.g. when changing pH).

Dansk resumé

I hele verden er svømmebassiner brugt til genoptræning samt rekreative og fysiske aktiviteter og derfor er det essentiel at vandet og luften i svømmehallen er sikkert for de badende og andre i hallen. Kloring er den mest udbredte metode til at kontrollere vandkvaliteten og til at hindre spredning af sygdomme mellem badende på grund af klors desinfektionseffekt. Udover den potentielle forurening med patogene mikroorganismer, bliver vandet forurenet med organisk og uorganisk materiale så som spyt, urin, sved og produkter til personlig pleje. Da klor er et stærk oxidationsmiddel, kan det oxidere forureningen i vandet og danne desinfektionsbiprodukter (DBPer). Der er identificeret mere end 100 forskellige biprodukter i svømmebadsvand, hvor nogle har vist sig at være genotoksiske og dermed muligvis medfører en øget risiko for kræft hos de badende.

Formålet med denne afhandling er at give et overblik over de strategier som kan anvendes til at opnå mikrobiologisk sikkert badevand med lavt niveau af DBPer for at sikre et sundt miljø for de badende.

Et sundt miljø for de badende kan opnås på forskellige måder, og i denne afhandling er de delt i følgende tre strategier: alternativer til klorering, fjernelse af forstadier og biprodukter, samt inhibering af dannelsen af biprodukter. Ingen af de alternative desinfektionsmidler, der benyttes i private svømmebassiner, er egnede i offentlige svømmebade. Dermed vil klor højst sandsynligvis også benyttes i offentlige svømmebade i fremtiden. Strategien med at fjerne forstadier og biprodukter inkluderer flere metoder: brusning af de badende inden svømning, filtrering, ozonering, brug af aktivt kul, stripning, og UV behandling. Generelt kan der opnås mindre badebelastning per bader ved at kræve brusning inden svømning og derved vil dannelsen af DPBer mindskes selvom tilførelsen af forstadier ikke kan fuldstændigt undgås. Hår og skinceller udgør forstadiemateriale for DBPer, og dermed vil god filtrering med hurtig fjernelse af partikler også være med til at sænke niveauet af dannede DBPer. Alternativt kan forstadiemateriale fjernes med ozon da ozonering af forstadier fører til organiske forbindelser der er mindre reaktiv med klor. Ozon kan også reagere med bunden klor og andre biprodukter, men reaktionen er langsom. Aktivt kul kan adsorbere forstadier og DBPer bortset fra kloramin, som fjernes katalytisk på overfladen af kullet. Dannelsen af biprodukter er uundgåelig. Flygtige biprodukter kan fjernes ved stripning, mens UV behandling hovedsagelig bruges til at kontrollere niveauet af bunden klor. Den sidste strategi med inhibering af biprodukt-dannelsen fokuserer hovedsaglig på pH, da ændringer i temperatur og klorkoncentration er begrænset på grund af komfort og sikkerhed for de badende.

I ph.d. studiet var formålet at undersøge muligheden for at fjerne andre biprodukter ved hjælp af UV behandling, der normalt bruges til fjernelse af bunden klor samt på at undersøge effekten af pH på dannelsen af udvalgte biprodukter.

Undersøgelserne blev udført i laboratorieopstillinger for at opnå kontrollerede forsøgsbetingelser. UV behandlingen kan fjerne en række biprodukter med varierende effektivitet. Generelt blev fotolyseeffektiviteten større ved udskiftning af klor med brom i biprodukterne. Bunden klor blev brugt som actinometer til at estimere den fjernelse af andre biprodukter, der kan forventes ved UV brugt til kontrol af bunden klor. Ved estimeringen blev der set bort fra andre fjernelsesprocesser. For meget flygtige biprodukter vil fjernelsen ved UV behandlingen have relative lav betydning for niveauet af biprodukterne medmindre de er meget sensitive for UV fotolyse (som f.eks. trikloronitrometan). For ikke-flygtige biprodukter er sensitiviteten for UV nedbrydning afgørende for at opnå en signifikant fjernelse. Konklusionen på undersøgelsen blev at der muligvis vil være signifikant fjernelse af trikloronitrometan, kloralhydrat og de bromholdige haloacetonitriller og trihalometaner som positiv sideeffekt af UV behandling til bunden klor kontrol i svømmebade.

Ændringer i pH-værdien i svømmebadsvand påvirkede de undersøgte biprodukter forskelligt. En analog bestående af hovedkomponenterne i urin og sved og partikler bestående af hår og hudceller blev anvendt som forstadiematerialer og ved begge typer af forstadiematerialer faldt dannelsen af trihalometan med faldende pH-værdi, mens haloacetonitrildannelsen blev forøget. Effekten af pH på dannelsen af haloeddikesyrer afhang af typen af forstadiemateriale. Partiklerne dannede ikke trikloramin ved klorering. Det gjorde kropsvæske analog derimod og dannelsen af trikloramin var meget afhængig af pH-værdien. Der var øget trikloramindannelse for pH under 7,0. Tilstedeværelse af bromid ændrede ikke pH's betydning for biproduktdannelsen, men der dannet mere af biprodukterne. Den estimerede toksicitet steg med faldende pH-værdi ligesom dannelsen af haloacetonitrillerne. I afvejning af hvilke biprodukter, der dannes, deres omfang og deres toksicitet, vil et optimalt pH område for svømmebade være pH 7,0 – 7,2 . Det skønnes dog, at effekten af pH på biproduktdannelsen i et lidt bredere interval (pH 6,8 – 7,5) er minimal, sammenlignet med andre faktorer som vil påvirke dannelsen af biprodukter i svømmebade.

Den fremtidige svømmehal vil bruge flere metoder til at minimere niveauet af DBPer i badevandet. De forskellige metoder skal optimeres sammen for at sikre den bedste vandkvalitet. Målet skal ikke være at minimere trihalometankoncentrationen da der dannes andre og mere toksiske biprodukter og at disse ikke altid følger samme tendens som trihalometanerne (f.eks. ved ændring i pH).

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List of abbreviations

The abbreviations found below are used throughout the thesis. They are presented by the full name followed by abbreviation in brackets the first time encountered and afterwards referred to by abbreviation.

Abbreviations	Full name
AOX	Adsorbable organic halogen
BFA	Body fluid analogue
DBP	Disinfection byproduct
EEO	Electrical energy per order
HAA	Haloacetic acid
HAN	Haloacetonitrile
THM	Trihalomethane
TOC/DOC	Total organic carbon / dissolved organic carbon
TON/DON	Total organic nitrogen / dissolved organic nitrogen

1 Introduction

There are approximately 850 public swimming pools in Denmark which are used for various purposes. Some of these activities are baby swimming, swimming lessons, physical activity and rehabilitation. Thus it is imperative that the water and air quality is maintained at safe levels to protect the health of bathers. Chlorination is the most frequently applied method in public pools for controlling pool water quality and for preventing spreading of pathogenic diseases among bathers because of its residual disinfection effect. However, it is well known that chlorine reacts with organic and inorganic matter in the swimming pool to form disinfection byproducts (DBPs) and that these DBPs can pose a health risk for the swimmers and lifeguards.

For a long time the research and regulation into DBPs from chlorination of pool water has been focused on trihalomethanes (THMs) and chloramines. Recent research has shown that the attention also should include other chlorinated molecules such as haloacetic acids (HAAs), haloacetonitriles (HANs), and halonitromethanes (Kramer et al., 2009; Richardson et al., 2010; Zwiener et al., 2007), since many of them are found to be genotoxic (Plewa et al., 2008) and thus may pose an increased risk to human health. Chlorination of drinking water and formation of DBPs has received considerable attention but the studies have limited applicability to pools due to the different type of organic matter. Furthermore, the system design for drinking water and pools is very different. The drinking water system is linear i.e. the water enter the treatment plant where it is treated and then send to the consumers. The swimming pool is a cyclic system. The water from the basin is treated and sent back to the pool basin again. Thus the DBP formation potential in drinking water and pool water will be different.

The overall aim of research within swimming pool water treatment is to identify conditions and techniques to ensure microbiological safe swimming pool water with low level of DBPs with focus on the most toxic ones. By achieving and implementing this, activities in swimming pools get even healthier than today.

1.1 Aim and approach

The overall aim of this PhD study was to contribute to the knowledge that is needed to ensure healthy swimming pools. Different strategies for pool water treatment were considered. In the beginning of the PhD study, the discussion of lowering the pH limit from pH 7.0 to pH 6.5 had started in Denmark. However,

the literature from drinking water indicated that there could be a problem with the formation of some DBPs. Furthermore, UV treatment is occasionally used in Denmark for combined chlorine control but there is a lack of knowledge of other processes occurring during UV treatment of pool water. Thus the focus of the PhD study has been on:

- The effect of pH on the formation of DBPs from different precursors and identification of optimal pH range.
- The possibility to remove DBPs with UV treatment and the risk of forming chloroform during the process.

These were achieved through laboratory scale experiments on the effect of pH, chlorine dose together with impact and effects of UV treatment on the DBP formation. Laboratory investigations were chosen to achieve controlled environment where the effect of changing a parameter could be studied.

The thesis gives an overview of strategies used to ensure a swimming pool environment (air and water) with lower levels of DBPs. The different strategies are discussed on the basis of literature study and the work performed during the PhD study. The structure of the thesis is as follows:

In Section 2, the general swimming pool system is described in short. The following section (Section 3) summarise the occurrence, regulation and health effects of DBPs. Section 3 is divided in two subsections covering the inorganic and the organic DBPs. Section 4 covers the strategies to obtain healthy environment in public swimming pools and is divided into three subsections. In the first subsection, alternatives to chlorine as disinfectant are discussed. The next subsection covers methods for removal of precursors and DBPs. The different methods are discussed based on literature and in the case of UV treatment results obtained during PhD study. In the final subsection, the possibility of inhibiting the DBP formation is discussed. Of the three main option (pH, reduction of chlorine concentration, and reduction of temperature) the focus is on the effect of pH which is discussed based on the results obtained in the PhD study.

2 Swimming pool systems

A swimming pool including the water treatment system consists generally of the following major parts: a pool basin, a circulation system with pumps and pipes, filters for filtration, system for online measurement and dosing of chlorine, pH adjustment, and heating of the water (Figure 1) (PWTAG, 2009).

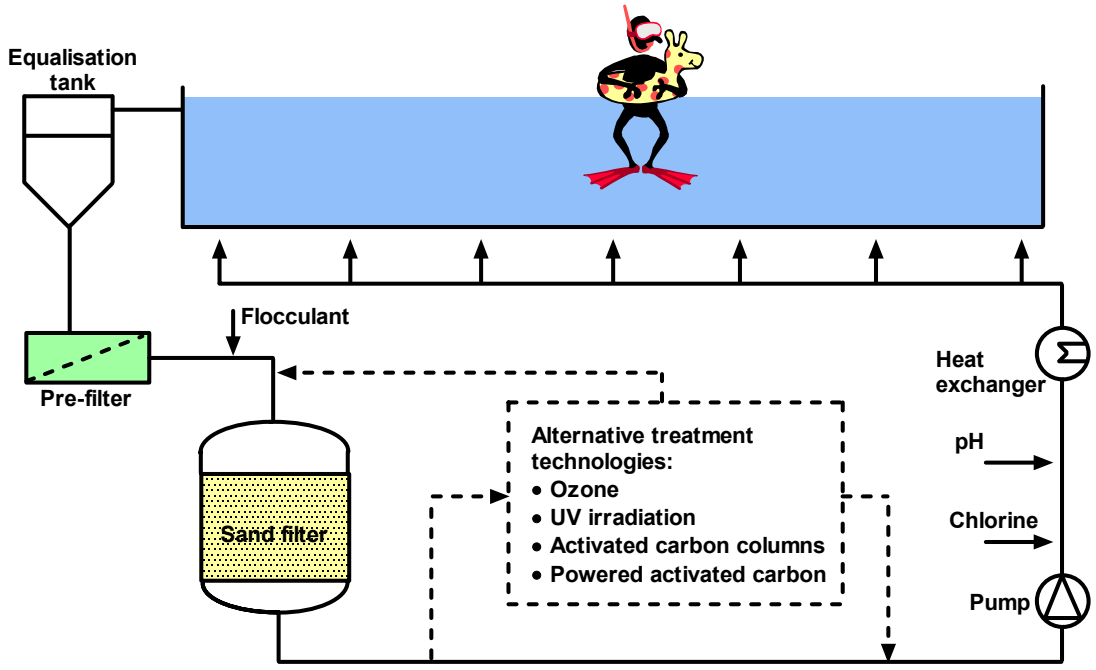

Figure 1. Schematic drawing of a swimming pool with water treatment system.

To ensure clean water there is a need for filtration of the water. The filtration should remove the particles added by the bathers. Sand filters are very common solution and is often used together with flocculation to remove the small particles as well. Other filtration techniques which are also used include zeolite filter, glass filter, membrane filter, and mesh-drum filter. The bathers might contaminate the water with *Cryptosporidium* when bathing while they are sick. Chlorine treatment is not efficient on killing *Cryptosporidium* oocysts and filtration is an effective way to reduce the spreading the oocysts (Hayes et al., 2009). Thus for all the used techniques it is important that the filters are able to remove particles, which is < 3 µm to ensure removal of *Cryptosporidium*. If that is not the case, a second barrier should be used which could be disinfection with UV on the entire recirculation stream.

Controlling and dosing chlorine and adjusting pH can either be done manually or by automated system. The automatic system is preferred (WHO, 2006) since it will continuously add chlorine to have constant level of free chlorine in the pool water. However, automatic systems are no guaranty against chlorine depletion

since sudden high bather load or poor design of the pool basin could result in local chlorine depletion (PWTAG, 2009).

Furthermore, many swimming pools use technologies for removal of combined chlorine, dissolved organic matter and/or organic byproducts. These technologies cover the use of UV irradiation, ozone, activated carbon columns either as full stream or side stream treatment and power activated carbon dosed on top of filters.

Accordingly, a pool system consists of many technological units; some are more advanced than others. The operation and performance of the different unit can affect the quality of the pool water both on microbiological and the level of DBPs. The occurrence, regulation and health effects of DBPs will be discussed in next section while the effect of some of the used technologies on the level of DBPs will be discussed in later sections.

3 Disinfection byproducts

Disinfection byproducts are defined as compounds formed when the disinfectant, chlorine, reacts with a precursor in the pool water. Thus the DBPs are an unwanted side effect of using chlorine to kill pathogens but difficult to avoid since chlorine is a strong oxidant. The precursors in the pool water are of very different sources and origins e.g. natural organic matter from filling water, different compounds in sweat and urine, soap, cosmetic products (make-up, lotion), and soil. The research knowledge within DBPs originates from identification and management of risk from DBPs in drinking water. The main difference in the precursors from drinking water and bathers is that anthropogenic DBP precursors are easier to oxidize and have higher carbon to nitrogen molar ratio than natural organic matter in drinking water (**Paper I**). The bathers are exposed to the DBPs through different routes. The main exposure routes are ingestion, inhalation and dermal sorption (WHO, 2006). Since some of the DBPs are volatile, the life guards and other personnel working in swimming pool area are exposed to DBPs though inhalation. The exposure to DBPs in swimming pools has lead to a concern of risk to the bathers' health.

DBPs can be divided into two main groups: the inorganic and organic DBPs. In the following, the occurrence, regulation and health effects of them will briefly be discussed.

3.1 Inorganic DBPs

3.1.1 Occurrence

The inorganic DBPs are a small group consisting of mono-, di-, and trichloramine also called chloramines. Furthermore, chlorate has been measured in pools and the levels in pools were found to relate to the levels in the hypochlorite stock solution (WHO, 2006). The chloramines were discovered in 1907 due to their disinfection power (White, 1992). In swimming pools mono- and dichloramine are formed from chlorine reacting with ammonium while trichloramine is formed from organic nitrogen where urea is one of the main precursors (Palin, 1950; Schmalz et al., 2011b; Stottmeister and Voigt, 2006).

The chloramines in the pool water are measured as combined chlorine which is a sum parameter measured with DPD (diethyl-p-phenylendiamine). The method quantifies both the inorganic and some organic chloramines (Li and Blatchley, 2007). Levels of combined chlorine have been reported between 0.01 – 0.49 mg/L as Cl_2 in a study of 92 German pools (Schmoll et al., 2009) and between

0.05 – 0.73 mg/L as Cl_2 in a study of 30 Swiss indoor swimming pools (Parrat et al., 2012). Trichloramine is volatile and can be measured in the air (Hery et al., 1995). Two recent papers have reported average values of trichloramine in air at 0.11 mg/m^3 (30 Swiss indoor pools; Parrat et al., 2012) and 0.21 mg/m^3 (10 Dutch indoor pools; Jacobs et al., 2012).

3.1.2 Health effects and regulations

The inorganic chloramines can cause odour problems and irritation of eyes and respiratory tract (Florentin et al., 2011; Wojtowicz, 2001) and thus many European countries have reference levels of combined chlorine (Schmoll et al., 2009). The WHO guideline recommend that the combined chlorine level should as low as possible and preferably less than 0.2 mg/L. Mono- and dichloramine are water soluble and monochloramine has been found to be more irritating for the eye than free chlorine while dichloramine was not tested (Chiswell and Wildsoet, 1989).

Trichloramine has a high vapour pressure and poor water solubility and consequently it evaporates from the pool water into the air (Schmalz et al., 2011b; Stottmeister and Voigt, 2006). Trichloramine has an odour similar to that of chlorine and since the odour threshold for trichloramine is a thousand time lower than chlorine it is often the cause of the "chlorine" smell in swimming pools (Stottmeister and Voigt, 2006 and Wojtowicz, 2001). Furthermore, trichloramine is suspected to increase risk of getting asthma but despite several studies have investigated the association of trichloramine with respiratory irritation or asthma (Bernard et al., 2007; Goodman and Hays, 2008; Hery et al., 1995; Jacobs et al., 2012; Massin et al., 1998; Thickett et al., 2002) there is still no definite conclusion. Common in most studies is that they have not measured the actual level of trichloramine which their test group was exposed to. A recent study performed an *in vitro* air exposure test using the human alveolar epithelial carcinoma cell line A-549 concluded that the concentration of trichloramine alone could not explain the inflammatory effect of air from an indoor swimming pool and that other volatile DBPs must also be contributing to the observed effects (Schmalz et al., 2011a).

Based on the finding of Hery et al. (1995), the WHO guideline (2006) recommends 0.5 mg/m^3 as limit for trichloramine in air while several countries in Europe have newer proposals with guideline value of trichloramine in the indoor air at 0.2 – 0.3 mg/m^3 (Cassan et al., 2011; Umweltbundesamtes, 2011).

In conclusion, combined chlorine is the DBPs are regulated in most countries. Trichloramine in air is the one parameter which most countries are in process of

including in the regulation at the moment. Regulatory levels of the DBPs are preferably set so the occurrence of known effects is none or very rare.

3.2 Organic DBPs

3.2.1 Occurrence

In 1974 both Rook (1974) and Bellar et al. (1974) reported their findings of the first organic byproduct, chloroform, formed during chlorination of drinking waters. In the following years other chlorinated compounds have been added to the list of DBPs found in chlorinated drinking water, e.g. haloketones (Suffet et al., 1976), haloacetonitriles (Oliver, 1983), haloacetic acids (Johnson et al., 1982), halonitromethanes (Thibaud et al., 1987). Today more than 600 different DBPs have been identified in chlorinated drinking water (Richardson, 2011) but the identified and quantified compounds only comprise approximately 30-50 % of the total organic halogens (Krasner et al., 2006; Richardson et al., 2007).

In an investigation of two outdoors pools, Zwiener et al. (2007) reported the findings of 18 different DBPs which consisted of some haloacetic acids, other haloacids, haloketons and a halosulfone. For most of these compounds it was the first time they were identified in swimming pool waters. A recent comprehensive study of two large indoor public swimming pools in Spain identified more than 100 DBPs (Richardson et al., 2010). Among the identified compounds, the number of nitrogen-containing DBPs was higher than typically found in chlorinated drinking water with several of the chemicals not identified in drinking water (Richardson et al., 2010). In a survey of 50 pools in France approximately 50 % of the total organic halogens were accounted for by the following DBP groups: trihalomethanes, haloacetic acids, haloacetonitriles and chloral hydrate (Brunet et al., 2010).

As seen in Table 1 chloroform is the most common THM but in some pools brominated THMs are found as well. Levels of chloroform from 0.5 to 298 µg/L have been reported in the literature. Reported levels of HAAs are given in Table 2. In general they can be found in quite high levels (17 – 1700 µg/L of trichloroacetic acid) since they are non-volatile under swimming pool conditions and the chlorinated acetic acids are stabile in present of chlorine at 25 °C (Heller-Grossman et al., 1993). Dichloroacetonitrile is the most common of the HANs and levels between 0.1 – 64 µg/L have been reported (Table 3). This is generally lower than the level of THMs which is most likely due to the instability of the HANs at neutral pH (Munch and Hautman, 1995; Oliver, 1983).

Table 1. Reported levels in indoor pools of trihalomethane in µg/L.

Country	Chloroform		Bromodichloromethane		Dibromochloromethane		Bromoform		Reference
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	
Denmark		15-40							Feilberg et al., 2007
		15-50							Feilberg et al., 2007
		90-160							Feilberg et al., 2007
		8-12							Feilberg et al., 2007
		15-25							Feilberg et al., 2007
		145-151							Kaas & Rudiengaard, 1987[a]
France	13	4-45	2	0.8-4.9	0.2	n.d.-1.2	n.d.		Brunet et al., 2010
	45	12-177	3.9	0.8-10	1.1	n.d.-2.2	0.3	n.d.-1.1	Brunet et al., 2010
USA	83	41-150	n/a	bdl-22	12	0.2-55	5.2	bdl-68	Weaver et al., 2009
	82	22-158	n/a	bdl-21	1.2	bdl-2.9	1.1	bdl-8	Weaver et al., 2009
	24	bdl-65	n/a	bdl-26	2	bdl-4.7	1	bdl-5	Weaver et al., 2009
	30	2-54	n/a	bdl-30	3.5	bdl-7.3	1.3	bdl-7	Weaver et al., 2009
	46	7-81	n/a	bdl-38	35	16-77	55	8.3-311	Weaver et al., 2009
	97	23-173	n/a	bdl-150	2.7	bdl-25	4.4	bdl-24	Weaver et al., 2009
	75	17-125	n/a	bdl-0.1	1.4	0.1-7.7	1.3	bdl-6	Weaver et al., 2009
	138	0.6-296	n/a	bdl-12	1.6	bdl-5.7	2.4	bdl-22	Weaver et al., 2009
	52	13-298	n/a	bdl-120	2.1	bdl-8.5	1.9	bdl-18	Weaver et al., 2009
	48	4.3-172	n/a	bdl-55	4	bdl -27	1.1	bdl-8	Weaver et al., 2009
Poland		36-100		2.3-15		0.2-0.8		0.2-203	Biziuk et al., 1993[a]
Italy		19-94							Aggazzotti et al., 1993[a]
	94	9-179							Aggazzotti et al., 1995[a]
	34	25-43	2.3	1.8-2.8	0.8	0.5-10	0.1	0.1	Aggazzotti et al., 1998[a]
USA	38								Copaken, 1990[a]
		4-402		1-72		<0.1-8		<0.1-1	Armstrong & Golden, 1986[a]
Germany		0.5-24		1.9-17		<0.1-3.4		<0.1-3.3	Ewers et al., 1987[a]
	95	41-118	4.8	4.2-5.4	1.8	0.8-2.6			Puchert et al., 1989[a]
	81		8.9		1.5		<0.1		Puchert, 1994[a]
		3-28		0.7-5.6		0.03-6.5		0.02-0.8	Cammann & Hübner, 1995[a]
		1.8-28		1.3-3.4		<0.1-1	<0.1		Jovanovic et al., 1995[a]
		8-11							Schössner & Koch, 1995[a]
	14	0.5-69	2.5	0.1-15	0.6	0.03-4.9	0.16	<0.03-8.1	Stottmeister, 1998, 1999[a]
		7-25							Erdinger et al., 2004[a]

Table 1. Continued.

Country	Chloroform		Bromodichloromethane		Dibromochloromethane		Bromoform		Reference
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	
Hungary	11	<2-62	2.9	<1-11					Borsányi, 1998[a]
UK	121	45-212	8.3	2.5-23	2.7	0.7-7	0.9	0.7-2	Chu & Nieuwenhuijsen, 2002[a]
Korea	21	n.d.-46	2.1	n.d.-7.0	n.d.		n.d.		Lee et al., 2010
	7.4	n.d.-21	1.1	n.d.-2.5	n.d.		n.d.		Lee et al., 2010

[a]values adopted from WHO guideline (WHO, 2006), n/a = not analysed, bdl. = below detection limit, n.d.= not detected.

Table 2. Reported levels in indoor pools of haloacetic acids in μg/L.

Country	CAA	DCAA	TCAA	BAA	DBAA	TBAA	BCAA	BDCAA	DBCAA	Reference
	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	
France	11	93	159		4					Brunet et al., 2010
	22	281	149		5.8					Brunet et al., 2010
Spain	4	45	155	n.d.	3	19	11	61	33	Sarrion et al., 2000
Spain	1000	n.d.	1700	n.d.	n.d.	n.d.	n.d.	480	n.d.	Loos & Barcelo, 2001
	15	n.d.	1500	n.d.	n.d.	n.d.	n.d.	912	62	Loos & Barcelo, 2001
	120	n.d.	1000	n.d.	n.d.	15	n.d.	208	n.d.	Loos & Barcelo, 2001
Spain	34	130	195	n.d.	1.4	n.d.	n.d.	3	n.d.	Cardador & Gallego, 2010
	42	94	55	n.d.	1.6	n.d.	n.d.	8	n.d.	Cardador & Gallego, 2010
Germany	26	23	42	0.3	0.6					Stottmeister & Naglitsch, 1996[a]
Korea		68	156							Lee et al., 2010
		12	17							Lee et al., 2010

CAA = chloroacetic acid, DCAA = dichloroacetic acid, TCAA = trichloroacetic acid, BAA = bromoacetic acid, DBAA = dibromoacetic acid, TBAA = tribromoacetic acid, BCAA = bromochloroacetic acid, BDCAA = bromodichloroacetic acid, DBCAA = dibromochloroacetic acid. [a]values adopted from WHO guideline (WHO, 2006), n.d. = not detected.

Table 3. Reported levels in indoor pools of haloacetonitriles in µg/L.

Country	DCAN		TCAN		BCAN		DBAN		Reference
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	
Denmark		1-5							Feilberg et al., 2007
		1-5							Feilberg et al., 2007
		20-25							Feilberg et al., 2007
		2-5							Feilberg et al., 2007
		2-7							Feilberg et al., 2007
France	35	15-64							Brunet et al., 2010
	25	4-120							Brunet et al., 2010
USA	8.6	1.5-21							Weaver et al., 2009
	10	5.0-18							Weaver et al., 2009
	7.9	4.7-14							Weaver et al., 2009
	7	4.3-11							Weaver et al., 2009
	15	6-31							Weaver et al., 2009
	31	7-87							Weaver et al., 2009
	8.6	2.1-24							Weaver et al., 2009
	14	0.6-45							Weaver et al., 2009
	15	7-44							Weaver et al., 2009
	20	1.8-47							Weaver et al., 2009
Germany		7-18							Puchert, 1994[a]
	13	0.1-148	1.7	<0.01-11		2.3	<0.01-24	14	Stottmeister, 1998, 1999[a]
	24								Baudisch et al., 1997[a]
Korea	3.9	0.5-12	n.d.		0.8	n.d.-1.9	0.5	n.d.-0.9	Lee et al., 2010
	1.3	0.2-3.2	n.d.		0.4	n.d.-0.6	0.4	n.d.-0.8	Lee et al., 2010

DCAN = Dichloroacetonitrile, TCAN = Trichloroacetonitrile, BCAN = Bromochloroacetonitrile, DBAN = Dibromoacetonitrile. [a]values adopted from WHO guideline (WHO, 2006), n.d. = not deteted.

Table 4. Reported levels in indoor pools of cyanogen halide and chloral hydrate in µg/L and TOC levels in mg/L.

Country	Cyanogen chloride		Cyanogen bromide		Chloral hydrate		TOC		Reference
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	
Denmark		10-50							Feilberg et al., 2007
		10-150						0.5-0.9	Feilberg et al., 2007
		100-250							Feilberg et al., 2007
		10-100						0.8-1.8	Feilberg et al., 2007
		15-400						0.4-0.7	Feilberg et al., 2007
France					156	53-250	3.1	1.8-4.9	Brunet et al., 2010
					237	69-497	3.9	2.3-7.3	Brunet et al., 2010
USA	3.6	0.5-26	3.9	0.3-8.7					Weaver et al., 2009
	4.2	1.0-12	3.6	bdl-8.6					Weaver et al., 2009
	6.7	1.1-55	3.6	0.7-11					Weaver et al., 2009
	2.8	0.6-16	3	0.7-4.8					Weaver et al., 2009
	17	0.9-176	31	bdl-325					Weaver et al., 2009
	5.1	0.5-16	8.2	bdl-23					Weaver et al., 2009
	3.0	0.1-26	7.6	0.5-26					Weaver et al., 2009
	4.8	bdl-41	11	bdl-55					Weaver et al., 2009
	12	0.5-132	8.4	0.8-36					Weaver et al., 2009
	10	0.04-194	9.3	2.1-18					Weaver et al., 2009
Germany						0.5-104			Mannschott et al., 1995[a]
					265				Baudisch et al., 1997[a]
Korea					17	5.1-35	2.3	0.5-7.0	Lee et al., 2010
					3.6	n.d.-10	1.7	0.7-3.9	Lee et al., 2010

[a]values adopted from WHO guideline (WHO, 2006), n/a = not analysed, bdl. = below detection limit, n.d. = not detected.

3.2.2 Health effects and regulations

The research within health effects of organic DBPs in swimming pools is very limited and most research on DBPs is performed due to their presence in chlorinated drinking water. As previously mentioned, chloroform was the first DBP identified and total THMs are together with combined chlorine the only DBPs which are regulated in Denmark. The level of total THMs is regulated in Denmark with maximum level at 25 µg/L (Statuary order no 623, 2012) while the limit in Germany is 20 µg/L (DIN 19643, 1997). None of the other organic DBPs are regulated in swimming pools.

It is very common to use THMs as an indicator of all DBPs and their formation in both regulations of chlorinated drinking water and swimming pools. However, chloroform is not carcinogenic to human by any exposure route in the levels typically found in drinking waters (Hrudey and Charrois, 2012). And in the effort to minimize the THM concentration in drinking water, the concentration of other DBPs which potentially are more harmful to human health could increase (Hrudey and Charrois, 2012). Likewise, recent research on DBP formation in swimming pool waters have shown that THM formation alone should not be used for evaluation of implementing new technologies or change of operation parameters in swimming pools (**Paper I; Paper II; Paper III**). Still, THMs could be used as evaluation of pool performance with regard to bather load.

The concern for the presence of DBPs is due to that several of the DBPs are found to be genotoxic (Richardson et al., 2007). Genotoxic substances cause damage to DNA but it does not tell whether humans will get cancer due to exposure. Villanueva et al. (2007) have reported an increased risk of bladder cancer associated with swimming pool attendances. Additionally, blood and urine samples taken from adults after swimming for 40 min in an indoor pool showed increased genotoxicity compared to the samples taken before swimming (Kogevinas et al., 2010).

In conclusion, the organic DBPs include many different compounds and the identification and quantificantion is not compleated and thus the ranging of which byproducts to be most concerned for is not done. The level of THMs is not the best parameter to use for optimisation of pool water treatment. Recent literature have used different kind of summarised toxicity tests (Kogevinas et al., 2010; Liviac et al., 2010; **Paper I**; **Paper II**; **Paper IV**; Schmalz et al., 2011a) to evaluate different parameters in swimming pools. Such summarised tests seem to be the best approach to evaluated heath risk from swimming at the moment.

4 Strategies

It is well known that DBPs are formed when chlorine reacts with dissolved organic carbon and nitrogen (illustrated in Figure 2). A common way to reduce the level of precursors and DBPs is to change water frequently. However, in Denmark the tax on water is high and the water is non-chlorinated and thus the filling water contains natural organic matter, which will form DBPs when chlorinated while in other counties water is a limit resource. Thus there is a wish for lower water change. Alternative strategies to prevent the formation of DBPs could be either removal of one or the other of the reactants or finding conditions where the reaction is inhibited. Since it is not the formation of DBPs it selves that is problematic but the exposure level, an additional solution could be to remove the DBPs or reduced the concentration of them. With this in mind the strategies for reducing DBP levels in swimming pools were divided into following three groups: alternatives to the use of chlorine, removal of precursors and the formed DBPs, and inhibition of DBP formation. In the following sections these strategies will be discussed.

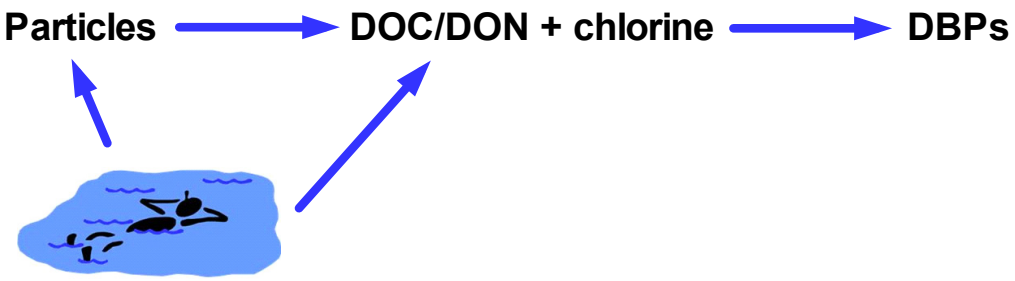

Figure 2. Formation of DBPs from dissolved organic carbon (DOC) and nitrogen (DON).

4.1 Alternatives to chlorination

Since the DBPs are formed when chlorine reacts with organic material choosing other disinfectant could be a possible solution to get rid of the DBPs. The Danish guideline and the German DIN standard have some common requirements for disinfectant used in public pools:

- Fast killing (Specified in the DIN: log 4 removal of *Pseudomonas aeruginosa* within 30 seconds).
- Sufficient residual effect to retain disinfection power from inlet to outlet of the pool.
- Preferably easy to use and control.

- Satisfactory difference between the concentration needed for disinfection and the one where health effects or discomfort for the bather occurs.

In the following, the alternative disinfection agents given in the box will be discussed.

Alternative disinfection agents which are used for private pools:

- Bromine
- UV light
- Hydrogen peroxide
- Copper and silver ions
- Ozone

In some countries bromine is used instead of chlorine. This will remove the smell of "chlorine" from the combined chlorine in pools since combined bromine is less volatile. However, a lot of byproducts are still formed (Richardson et al., 2010) and in general the bromated byproducts are much more toxic than their equivalent chlorinated by-product (Muellner et al., 2007; Plewa et al., 2002; Plewa et al., 2008). So operating swimming pools with bromine as disinfectant is not less problematic regarding formation of DBPs and increased toxicity of the pool water is the most likely scenario.

UV light is used for disinfection of drinking water and effluents from sewage plants. Microorganisms are inactivated due to damaged DNA which disrupts the ability to replicate (Bolton, 2010). However, UV light does not leave any residual disinfection in the water and there will be no protection of the bathers in the pool from pathogenic diseases. Thus UV light is not an alternative to chlorine as primary disinfectant.

Another possibility is hydrogen peroxide. A few public swimming pools are using hydrogen peroxide e.g. Lund and Bjärnum swimming pool in Sweden (Vila, 2006), which are able to maintain biologically requirements with approximately 80 mg/L H_2O_2. A Dutch pool was experimentally operating with 50-60 mg/L H_2O_2, but had to close after short time due to problems with the filters and unsatisfactory biologically water quality (Calders, 2005). A recent paper reported that hydrogen peroxide at a concentration of 150 mg/L has less than 1 log removal within 30 seconds of five different micro-organisms (including *Pseudomonas aeruginosa*) and even after 30 min the log removal was still less than 1 (Borgmann-Strahsen, 2003). Thus hydrogen peroxide does not appear as

an alternative to chlorine in public swimming pools from a microbiological point of view.

Commercial products for disinfection based on copper and silver ions are available for private swimming pools. However, the contact time needed is in the order of hours to achieve the same inactivation of several micro-organisms which chlorine kills within seconds or minutes (Falk, 2010). Thus silver and copper ions do not fulfil the requirements for use in public swimming pools. Silver and copper ions can be used in combination with chlorine; however there is a lack of well documented investigations (Kristensen et al., 2007a).

Ozone is a very effective disinfectant and is even able to inactivate *Giardia* and *Cryptosporidium* where chlorine falls short (WHO, 2006). Ozone is a volatile gas with low solubility at 25-30 °C (Rice, 1995). Furthermore, ozone (g) is toxic and heavier than air (WHO, 2006). Thus it would be difficult to obtain a sufficient ozone concentration in the pool water near the surface without having ozone in the air. The guideline value for ozone in indoor air is 0.1 ppm (Danish Working Environment Authority, 2012).

The mentioned alternative disinfectants are all failing in one or more of the criteria given in the beginning of this section. Consequently, none of them can be used as an alternative to chlorine for disinfection in public pools.

4.2 Removal of precursors and DBPs

Since chlorine is the current and most likely future scenario as disinfectant, other ways to reduce the levels of DBPs is needed. One approach could be to remove or minimizing the amount of precursors. Another approach would be to remove some of the DBPs. The methods which will be discussed in this section and their main target are shown in Figure 3.

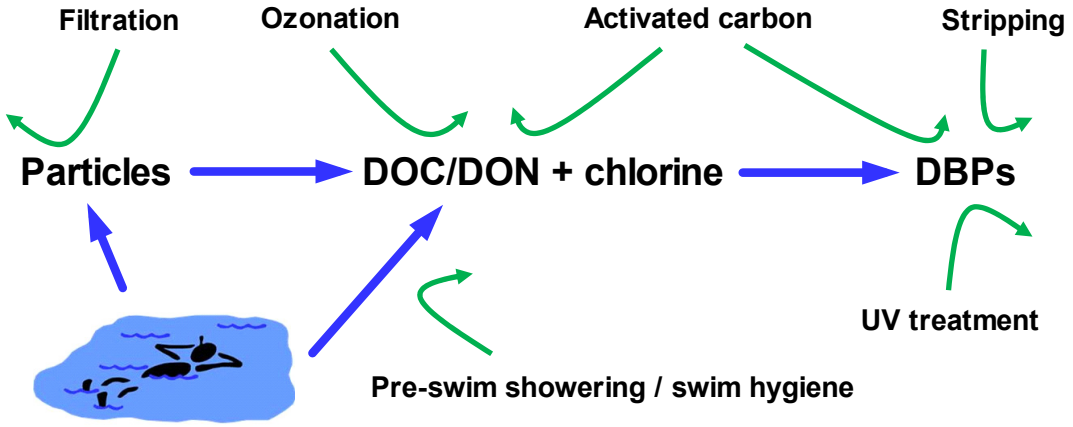

Figure 3. Methods for removal of precursor and DBPs.

4.2.1 Importance of pre-swim showering and swimming hygiene

Beside killing bacteria chlorine is also used to oxidize organic matter added by the bathers (Rice, 1995). And more organic matter means more chlorine is needed to maintain residual chlorine in the pool water (Judd and Bullock, 2003; PWTAG, 2009). The research within effect of bather load is very limited and the knowledge and recommendations are mainly based on experience from pool operators. A study of precursor load in a test pool (scaled model) observed increased chlorine consumption and combined chlorine level when the precursor level was increased (Judd and Bullock, 2003).

Since the main load of precursors is added by the bathers, a good hygiene both pre-swim and during swimming is important. Keuten et al. (2012) have determined that most of the pollutant was released during the first 1 minute of showering. And thereby load of precursors can be reduced significantly by pre-swim shower. However, it is very culture depended whether people takes shower before swimming in a pool. In UK, showering is more seen as a mean of washing of the pool water (PWTAG, 2009) and in a survey 25 % of pool users admitted not taking a pre-swim shower (Swimming Teachers Association, 2012). Encouraging bather not to urinate in the pool water on purpose will decrease the bather load as well.

It is difficult to change people's behaviour. In 2009 a survey by the Water Quality & Health Council in USA resulted in widespread public interest and media coverage since 17 % of respondents admitted urinating in the public pool. However, in the next survey in 2012 there was no change in the number of bathers admitting urinating in the pool water (Wiant, 2012).

4.2.2 Filtration of particles

Besides soluble matter, the bathers add particles to the pool water consisting of mainly skin cells. A small Danish study counted the particles in the water of a spa with the same persons in it for one hour and found that the release was continuously as the particle account increased linear with time (Klausen, 2010). Generally, particles are collected on top of the filters where the particles are continuously exposed to chlorinated water. The continuous exposure leads to hydrolysis and chlorination of the particles which results in formation of DBPs. Erdinger and Masher (2011) have found that the initial water from back washing a sand filter had higher THM formation potential than the pool water itself. The formation potential of the back wash water decreased with back washing time as the filter was cleaned (Erdinger and Mascher, 2011). It is presumed that there is a correlation between time or chlorine exposure and DBP formation. Particles

collected with a drum filter from a spa had short chlorine contact time before removal. The particles were found to form chloroform, di- and trichloroacetinitrile, and di- and trichloroacetic acid (Figure 4 and **Paper II**) after 48 hours of chlorination at 25 °C. The particles were tested for trichloramine formation at pH 6.0 but the formation was negligible (approximately at the quantification limit of 0.8 µmol/L) (**Paper II**).

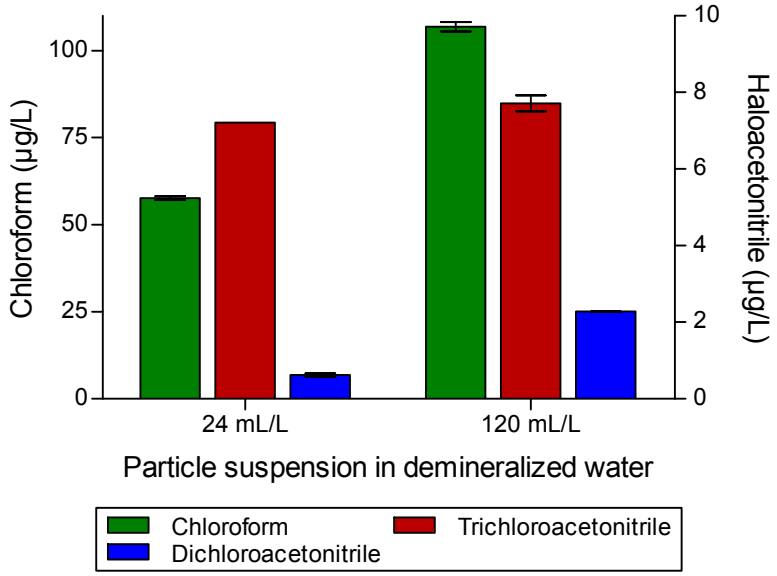

Figure 4. Formation of DBPs after chlorination of filter particles. The particle suspension was collected from a drum filter installed at a spa. Experimental condition: pH = 6.0, chlorine concentration = 35 mg/L, temperature = 25 °C and reaction time = 48 hours. Data from design experiment for **Paper II**.

Fast removal of the particles e.g. with drum filter or membrane filters, could be a possible way to reduce the level of organic DBPs which is formed, while it will have no effect on the level of trichloramine.

4.2.3 Ozonation

Ozone is a chemical oxidizing agent which can be used as a part of the pool water treatment. Ozone reacts rapidly with unsaturated organic compounds and phenolic compounds (White, 1992), while the majority of organic compounds react slowly with ozone and are only partly oxidized (Rice, 1995). The partial oxidation results in organic compounds with more polar groups such as carbonyl (>C=O), carboxyl (-COOH), and hydroxyl (-OH). The polar compounds can form complex together with polyvalent cations (microflocculation) which can be removed with filtration (Rice, 1995). The reaction of polar organic groups with chlorine is very slow (Deborde and von Gunten, 2008) and thus the DBP formation will be reduced.

Ozone is not likely to react with most DBPs and would mainly be a technique to remove precursors. However, chloramines have been found to react slow with ozone to form nitrate and chloride ions (Eichelsdorfer and Jandik, 1985; Eichelsdorfer and Jandik, 1988; Rice, 1995).

The important precursor for trichloramine, urea, can react with ozone to form nitrate and ammonia, however the reaction is very slow (Eichelsdorfer and Jandik, 1985). Other nitrogen-containing organic compounds also react very slowly with ozone while the nitrogen-chloro-derivatives (e.g. chlorurea, and chloramino acids) are easier to oxidize with ozone (Rice, 1995).

In a study carried out in South Korea, the level of DBPs in 30 indoor swimming pools disinfected with chlorine and 30 pools with chlorine/ozone was investigated. It was found that the average concentration of THMs, HAAs, HANs, and chloral hydrate were significantly lower when disinfection with chlorine/ozone compared to only chlorine (Lee et al., 2010). Furthermore, short ozonation of pool water (2-3 min of contact time) was able to reduce THM formation potential while increased contact time (15 min of contact time) resulted in further reduction of the formation potential (Eichelsdorfer and Jandik, 1988). Beside reduction of THM formation potential, Glauner et al. (2005) also found a reduction of absorbable organic halogen (AOX) and AOX formation potential and a slight reduction in TOC level in swimming pool water after 10 minutes of ozonation.

4.2.4 Stripping of volatile DBPs

Many DBPs are volatile and that property may be used to reduce the level of them in the pool. If installing a trickle bed reactor as part of the water treatment, it is able to strip the volatile DBPs. A trickle bed reactor installed in connection to a small warm water pool reduced the chloroform level in the pool with almost 40 % compared to a reference period without stripping (Kristensen et al., 2010). The trickle bed reactor does not change the THM formation potential, the AOX level or the AOX formation potential (Kristensen et al., 2010). This is as expected since the reactor only is stripping the DBPs and is not removing precursors. During the experiment only chloroform was measured, but other volatile DBPs such as trichloramine and HANs are expected to be removed as well.

4.2.5 UV photolysis of DBPs

Treatment with ultraviolet light has for some years been used for control of combined chlorine concentration (PWTAG, 2009). In 1976 the first medium

pressure UV system was installed in a swimming pool in Denmark and today there are estimated to be 1000-2000 installations in public pools in Europe (Povl Kaas, Personal communication). In general, UV photolysis is driven by absorption of light in a molecule so the molecule gets excited which might results in breaking of the bonds (Bolton, 2010). An example is given for monochloramine in Equation 1 (Kaas and Andersen, 2007).

$$NH_2Cl \xrightarrow{h\nu} NH_2Cl^* \longrightarrow N_2 + H^+ + Cl^- + \ldots \quad (1)$$

Several full scale studies have reported reduction of combined chlorine level when treating with medium pressure UV lamps (Beyer et al., 2004; Cassan et al., 2006; Cassan et al., 2011; Kristensen et al., 2009). Furthermore, Cassan et al. (2011) have reported up to 32% reduction of trichloramine in air using full stream medium pressure UV treatment. However, these studies are not in alignment concerning the effect of UV on THM formation. Cassan et al. (2006) found increase THM levels in the pool water while Beyer et al. (2004) report a decrease in THM levels in a similar study. In a long term study including matched control periods with and without UV treatment in a public pool, Kristensen et al. (2009) showed no effect on THM levels in a swimming pool treated by several types of UV treatment. Glauner et al. (2005) have found increased THM formation potential in pool water treated with UV in laboratory setup, which might explain the different observation as in some cases the THM formation potential will turn into THMs while not in others. The UV treatment is able to remove precursors. At low UV dose the removal would be too small to be detected. A study with very high UV dose reported that the THM level was increased in the beginning but then decreased as the precursors were removed (Kristensen et al., 2010). Furthermore, in full scale the grab sampling for THM analysis should be planned carefully since the concentration of THMs can vary with approximately 50 % during a day being highest in the morning and lowest in the evening (Kristensen et al., 2009).

In laboratory setups specific mechanisms can be investigated under more controlled environment. However, there is a need for a method to convert the exposure time in the laboratory setup to the UV dose in the full scale system. The characterisation of UV lamps is traditionally performed by determining the fluence (UV dose, in mJ/cm^2), but this works best for low pressure lamps where the light is primarily emitted at 254 nm and the quantum yields for the different actinometers are well known. The determination of fluence for medium pressure lamps which have broad spectral outputs is considerably more complicated,

requiring the use of a table of wavelength spectral specific absorbances and quantum yields.

The international union of pure and applied chemistry (IUPAC) advises the characterisation of UV systems for removal of chemicals by either direct photolysis or advanced oxidation to be conducted by energy consumption (Bolton, 2010). They recommend using the Figure-of-Merit, the electrical energy per order (EEO) when the photodegradation follows first order kinetics, which generally is found at low concentrations. The EEO is defined as the electrical energy consumed per unit volume of water treated required for 90 % removal of the investigated compound (Bolton, 2010) and can be calculated from the expression:

$$\log\left(\frac{C_{out}}{C_{in}}\right) = \frac{-1}{EEO} \cdot EED \qquad (2)$$

Where Cin and Cout is the concentration of a compound in the inlet and outlet, respectively, EEO is the electrical energy per order and EED is the electrical energy dose.

To relate the UV exposure/dose given in a laboratory setup with UV dose in a real treatment situation in swimming pool, naturally occurring combined chlorine has been used as an actinometer in a recent paper (**Paper III**).

In full scale UV system different UV doses was achieved by varying the water flow through the UV system and the electrical energy consumption for the treatment, determined by the number of lamps turned on. The concentration of the free and naturally occurring combined chlorine was measured before and after the UV reactors with different UV doses. The EEO for free chlorine and combined chlorine in Gladsaxe swimming pool was determined to be 0.22 kWh/m^3 and 1.0 kWh/m^3, respectively.

In laboratory scale the irradiation time to achieve 90 % removal of combined chlorine was 10.5 min, corresponding to the energy dose at EEO. In Gladsaxe swimming pool (i.e. full scale treatment) the EEO for removal of combined chlorine was 1.0 kWh/m^3. Thus the EEO of 10.5 min in the collimated beam was estimated to be equal to the EEO of 1.0 kWh/m^3 in the swimming pool and thereby 1.0 min irradiation time in the collimated beam setup was calculated to be equal to 0.095 kWh/m^3 in the full scale treatment system. This estimation was used to predict the approximate value of EEO for the investigated DBPs.

The removal of 12 common organic DBPs was investigated using collimated beam setup with a medium pressure UV lamp. The possible formation of any of

the investigated DBP from organic matrix in swimming pool water was avoided by performing the experiment on pure chemicals in solution of purified water. The photolytic removal rate of DBPs was successfully fitted to an integrated first order kinetic expression. Selected examples can be seen in Figure 5.

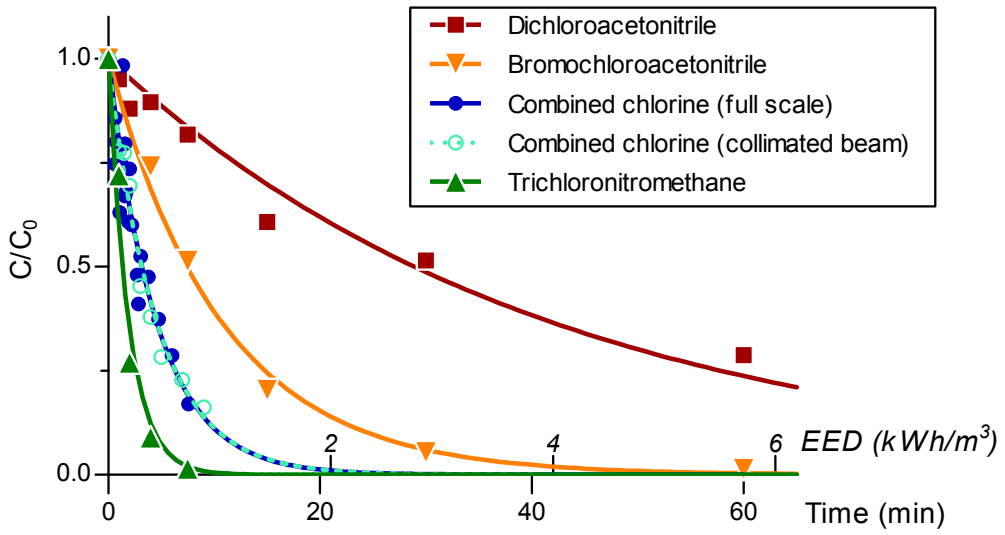

Figure 5. Photolytical removal of selected DBPs and the fitted lines according to first order kinetic. The second horizontal axis (italics) indicates the estimated equivalent energy in full scale treatment. Modified from **Paper III**.

The presence of bromine in the molecular structure of THM remarkably increased the removal rate (**Paper III**), since these species are more photosensitive than their chlorinated analogues (Chen et al., 2010; De Laat and Berne, 2009; Lekkas and Nikolaou, 2004). This effect of bromine incorporation on the photosensitivity was found for the HANs as well (Figure 5, **Paper III**).

The values of EEO were estimated based on the conversion of irradiation time to electrical energy dose and with the use of Equation 1. The obtained values of EEO ranged from 0.4 kWh/m^3 (trichloronitromethane) to 12 kWh/m^3 (dichloropropanone) (**Paper III**). Thus trichloronitromethane was the easiest to remove of the 12 organic DBPs investigated, as a high value indicates that a large amount of energy is required to remove a compound.

The UV system in the warm water pool in Gladsaxe swimming pool consisted of 4 UV lamps (each 0.7 kW) running 24 h per day with a total pool volume of 50 m^3. This gives an applied electrical energy dose from UV of 1.34 kWh/(m^3·d^1). Considering UV treatment as the only removal process affecting the investigated DBPs, the removal (1-C_{out}/C_{in}) achieved by applying UV treatment in a real swimming pool can be estimated using Eq. 1. Chloroform, dichloroacetonotrile, and di- and trichloropropanone can be expected to exhibit a removal of less than 30 % of the initial concentration per day whilst the rest of the investigated DBPs

are expected to exhibit more than 63 % removal, with some being on 100 % of the initial concentration per day (Figure 6).

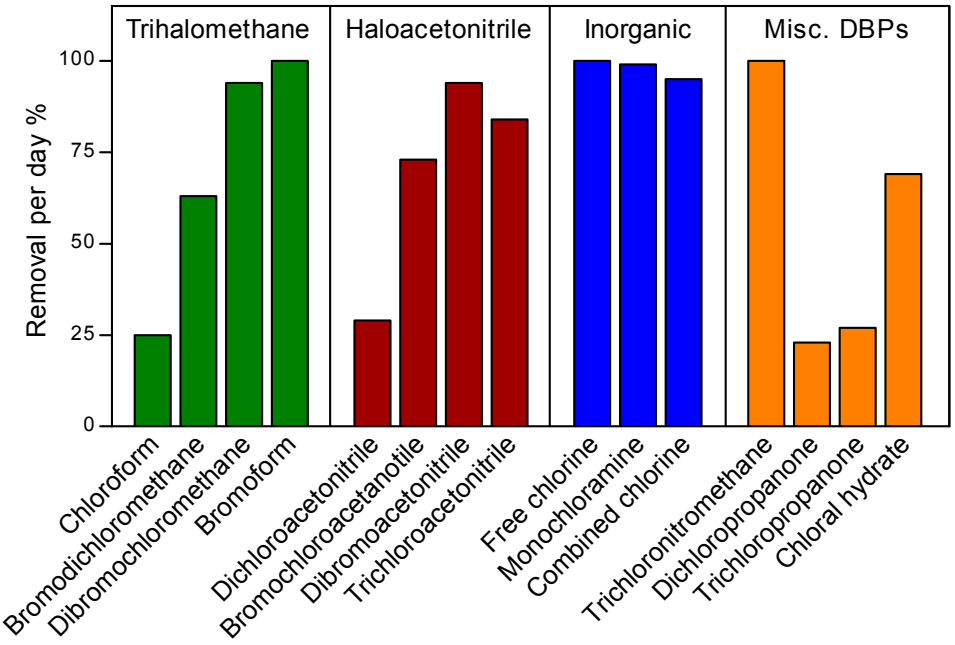

Figure 6. The removal of DBPs estimated for a pool with a UV treatment dose of 1.34 kWh/(m^3·d) considering UV as the only removal process. Data from **Paper III**.

It was predicted that 95 % of the combined chlorine concentration could be removed by UV treatment in one day. However, in a swimming pool setting other processes than UV treatment such as formation, volatilisation and degradation will affect the concentration of combined chlorine and the other DBPs. So, in a test of the UV system in Gladsaxe swimming pool over several weeks a decrease of 67 % in the steady state concentration of combined chlorine in the pool basin was achieved (Kristensen et al., 2009; Kristensen et al., 2010) which is less than the predicted 95 %. For the very volatile DBPs, such as chloroform and trichloroacetonitrile, it can be expected that photolysis has a relatively low importance for the fate of the DBPs compared to the volatilisation. Conversely, chloral hydrate is very stable in pool water because it hydrolyzes very slowly at neutral pH, reacts slowly with chlorine, and is not volatile (Brunet et al., 2010) and since it is photolysed at a medium rate UV treatment could decrease the concentration of chloral hydrate in swimming pools.

In conclusion, treatment with UV is able to remove combined chlorine and when installed in swimming pools UV systems are able to lower the level of combined chlorine in the pool water. A positive side effect of UV for combined chlorine

control might be removal of trichloronitromethane, chloral hydrate and the bromine containing haloacetonitriles and trihalomethanes (**Paper III**).

4.2.6 Activated carbon

Activated carbon is widely used in swimming pools to remove combined chlorine. Combined chlorine is not adsorbed in the filter but removed due to catalytic reaction at the surface of the activated carbon (Bauer and Snoeyink, 1973). Both monochloramine and dichloramine are oxidized to N_2 on the surface of the activated carbon (Bauer and Snoeyink, 1973). Free chlorine is also removed by catalytic reaction at the surface of activated carbon. Uhl and Hartmann (2005) have found that combined chlorine is removed slower than free chlorine and thus is penetrating deeper into a granulated activated carbon filter. The removal efficiency will decrease with operation time (Skibinski et al., 2009; Uhl and Hartmann, 2005). Activated carbon filters are able to absorb most organic precursors and DBPs (DIN 19643, 1997). Some studies found increased chloroform concentration after carbon filter (Feilberg et al., 2007; Uhl and Hartmann, 2005). A likely explanation is that chlorine reacts with the adsorbed precursors which have been reported with humic substance adsorbed on granulated carbon (McCreary and Snoeyink, 1981).

Due to the removal of free chlorine there is a risk of microbiological growth in granular activated carbon filters. Uhl and Hartmann (2005) have reported a decrease in assimilable organic carbon and an increase in the heterotrophic plate count after filter beds with granulated activated carbon. The effluent from the pilot filters were tested positive for *Pseudomonas aeruginosa* and back wash with chlorine (1.0 or 2.0 mg/L) was found insufficient to remove the contamination (Uhl and Hartmann, 2005).

Activated carbon may also be used as powder which is injected as a thin layer on top of the sand filter (DIN 19643, 1997). The powdered activated carbon is then replaced at every back flush of the sand filter. This way there is frequently change of activated carbon which can absorb THMs and other DBPs and the risk of microbiological growth is minimal.

4.3 Inhibition of the DBP formation

Another way to minimize the DBP formation is to identify conditions where the formation reactions are limited. In general, decreased temperature, chlorine level, and change in pH could decrease the formation. However, in reality the possibility to change these parameters is limited in swimming pools due to

comfort and safety of the bather. The temperature in pools for training and competitive swimming is generally at 27 - 29 °C, while the temperature is a bit higher for leisure pools and pools for baby swimming and rehabilitation (30 - 32 °C) (PWTAG, 2009). In Denmark the free chlorine concentration in the pool has to be between 0.4 and 1.5 mg/L (Statuary order no 623, 2012). The chlorine level depends on the water treatment system (such as the age of the pool and how well the pool is operated) and the pH level of the pool water as well. Chlorine exhibits a pH and temperature dependent-equilibrium between the hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-) ($pK_{a,25°C}$ = 7.5) (White, 1992) which means that at pH 7.5 there is 50 % of HOCl and 50 % of OCl^- (See Figure 7). HOCl is the main active species responsible for the disinfection effect of chlorine (White, 1992). Thus one way to limit the formation of some DBPs could be to reduce the chlorine concentration as well as the pool water pH, so HOCl concentration is maintained thus maintaining the disinfection efficiency.

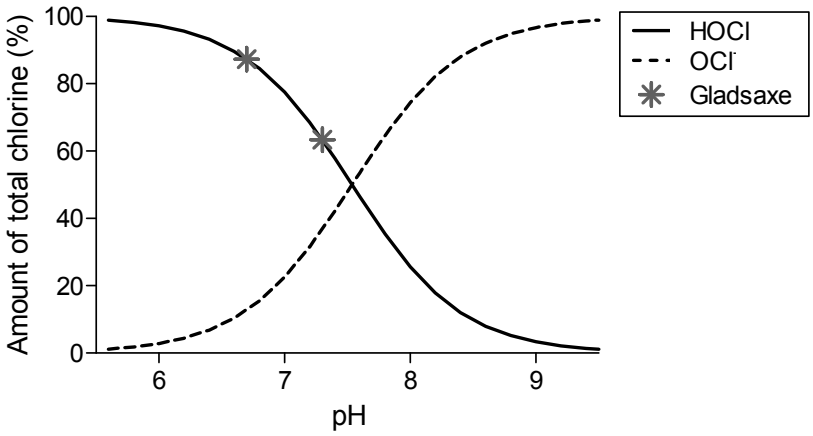

Figure 7. The distribution of HOCl and OCl^- due to dissociation. The crosses indicate the pH values which were compared in a study in Gladsaxe done by Kristensen et al. (2007b).

The validity of this assumption is supported by a Danish full scale study on a public indoor warm water pool, where the DBP formation at pH 6.7 and 0.4 mg/L of chlorine were compared to the traditional pH at 7.3 with 1.5 mg/L of chlorine (pH marked in Figure 7). The study reported a decrease in the level of THMs, AOX and combined chlorine while microbiological quality was maintained at the lower pH (Kristensen et al., 2007b).

The effect of pH on DBP formation and how to test it in laboratory scale experiments will be discussed in the following subsections.

4.3.1 Experimental design to investigate pH effects

To investigate several values of pH in full scale swimming pools it would take considerably time where one would have to cope with many uncertainties. In laboratory scale batch experiment several levels of pH can be investigated at the same time under controlled conditions. Such a simulation test with the aim to quantify the production of volatile DBPs is ideally performed under realistic conditions with continuous low chlorine concentration for long time. Unfortunately, DBPs such as HANs are not stable in water over timescales of several weeks (Munch and Hautman, 1995; Oliver, 1983). This suggests that a simulation test needs to be made as an accelerated test with high chlorine concentration for short time where the DBPs are formed in a suitable level to identify a change in DBP formation. This approach has been used by several authors in recent papers (Kanan, 2010; Kanan and Karanfil, 2011; Kim et al., 2002; Li and Blatchley, 2007; **Paper I**; **Paper II**; **Paper IV**; Schmalz et al., 2011b).

In such a simulation test the high ratio between chlorine:organic matter may cause a shift in the byproduct profile. The effect of chlorine dosing on the DBPs formation has been investigated by Hansen et al. (**Paper I** and **Paper IV**) and Kanan (2010). The chlorine could either be added as one initial dose or as a similar dose but divided over time. Hansen et al. (**Paper IV**) found that the two approach gave different concentration profiles of chlorine (Figure 8a) but after 48 hours the chlorine consumption was approximately 70 % of total dose in both cases (Figure 8b). Furthermore, there was no correlation between pH and chlorine consumption. Additionally, the addition of chlorine as an initial high dose or several small doses has relative small effect on the formation of chloroform and dichloroacetonitrile (Figure 8c). However, uncapping the bottles during the experiment in order to add chlorine increased the uncertainty of the results.

The effect of the ratio between chlorine dose and TOC on the DBP formation was investigated in both in Kanan (2010) and in **Paper I** and in both cases where the formation of chloroform increasing when chlorine:TOC ratio increased. The HAA formation increased as well when the chlorine:TOC ratio increased (Kanan, 2010). The formation of HANs varies a lot with the chlorine dose. At low chlorine dose (10 mg/L) dichloractetonitrile was formed, however when chlorine dose increased trichloroacetonitrile was formed instead (Figure 8d). At high chlorine doses (35 mg/L) di- and trichloroacetonitrile formation decreased but chloroform formation increased.

In conclusion, the accelerated test cannot be used for predicting the level of the different DBPs in swimming pools since the DBP formation is affected by the chlorine:TOC ratio. The test can be used for testing different parameters such as pH and bromide incorporation.

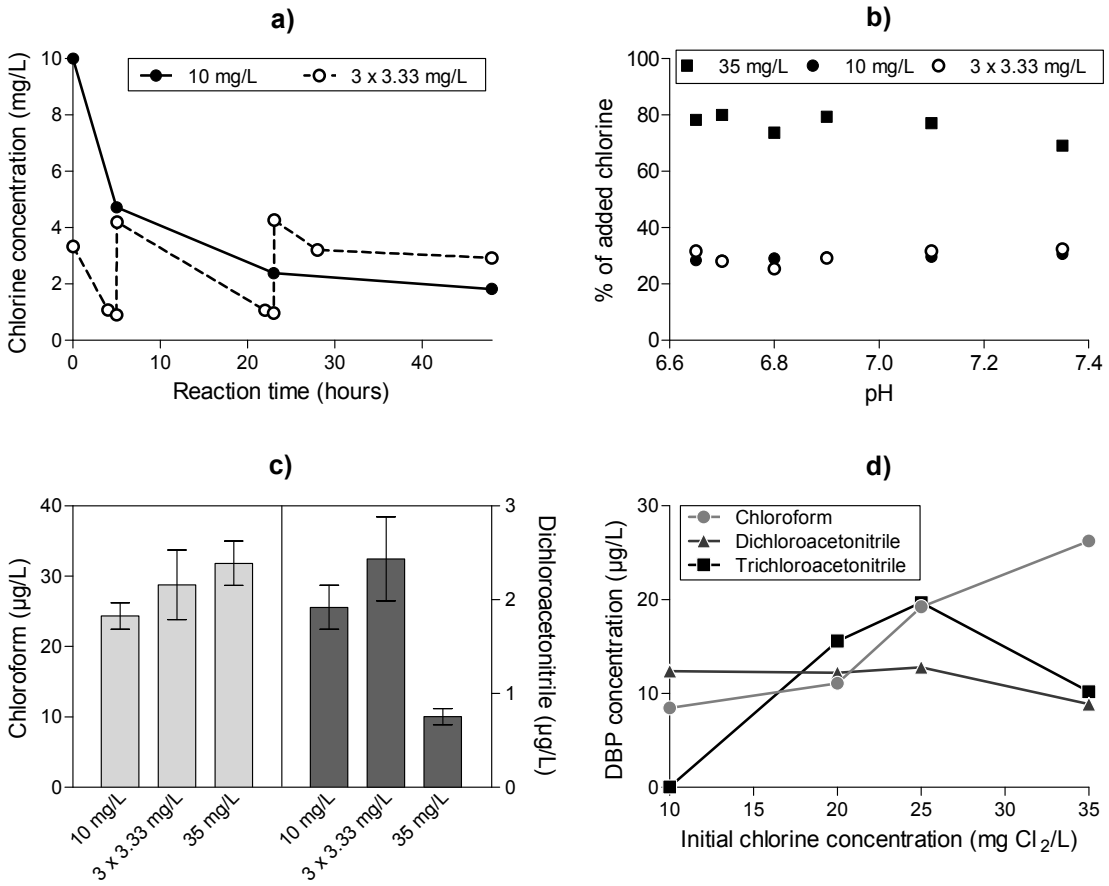

Figure 8. Effect of chlorination method on chlorine concentration and DBP formation. a) Profiles of chlorine concentration at pH 6.9. b) Concentration of free chlorine after 48 hours as % of the added chlorine. c) DBP formation at pH 7.5, error bars = standard deviation d) Effect of initial chlorine concentration on DBP formation at pH 6.0. Experimental condition: body fluid analogue addition = 1 mg TOC/L, reaction time = 48 h. Data from **Paper I** and **Paper IV**.

Besides appropriate chlorine dosing, realistic precursor material is important. As previously mentioned, bathers add both soluble and particular matter to the swimming pool water. To simulate the soluble part of the bather load different artificial analogue has been used in recent literature (Judd and Bullock, 2003; Kanan and Karanfil, 2011; **Paper I**; **Paper IV**). The analogues are generally consisting of main compounds in sweat and urine and are referred to as body fluid analogue (BFA). The particular matter mainly consists of hair and skin cells. Kim et al. have used hair and skin collected from a man in their investigation where Hansen et al. (**Paper II**) collected particle as a suspension from a drum filter installed at a spa.

Some researcher (Kanan, 2010; Kim et al., 2002) have mixed the anthropogenic precursors with drinking water in the attempt to make a simulation of swimming pool water. However, in that case it can be difficult to separate the effects on the DBP formation from the drinking water and the precursors.

4.3.2 The effect of pH on organic DBP formation

Since chlorine exhibits this pH depended dissociation between hypochloric acid and hypochlorite, two different chlorination approaches have been used to investigate the pH effect on DBP formation in **Paper I** and **Paper II**. One approach was to keep free chlorine constant at the investigated pH values. The other approach was to keep the active chlorine i.e. HOCl concentration constant by varying the free chlorine concentration depending on the pH. The results from **Paper I** and **Paper II** are summarised in Figure 9. From the two chlorination approaches it can be concluded that the HAA formation was affected by the change in chlorine concentration occurring with the two approaches while there was found no significant difference between the two approaches on the formation of THMs and HANs, except for HANs at pH 8.0 (Figure 9a, c, e vs b, d, and f). At pH 8.0 a high concentration of chlorine was needed to maintain the same level of active chlorine as pH 7.0. This combination of high pH and very high free chlorine is unrealistic for swimming pools since the increasing concentration of OCl^- would contribute to the disinfection power allowing an equivalent disinfection power at a lower total chlorine concentration (White, 1992) and the high free chlorine would have other undesired effects for swimmers.

The change in pH affected the formation of the investigated DBP groups differently (Figure 9). Specifically, THM formation increased with increasing pH for chlorination of both body fluid analogue and particles. The same pH dependency have been reported in a study with mixture of BFA and drinking water (Kanan, 2010) as well as studies on chlorination of drinking waters (Bougeard et al., 2008; Liang and Singer, 2003). For both the body fluid analogue and particle suspension HAN formation was favoured at low pH and decreased with increasing pH. At chlorination of body fluid analogue there was found no effect of pH on the formation of HAAs whereas at chlorination of particles there was found an increase from pH 6.0 to pH 7.0. Some drinking water studies reported increasing HAA concentration with decreasing pH (Cowman and Singer, 1996; Liang and Singer, 2003) while others found contradictory pH dependencies for two different types of drinking water (Bougeard et al., 2008). Kanan (2010) has reported increased HAA formation with increasing pH for a mixture of BFA and drinking water. Based on these

findings, it can be concluded that the pH effect on the HAA formation strongly depends on the precursor material.

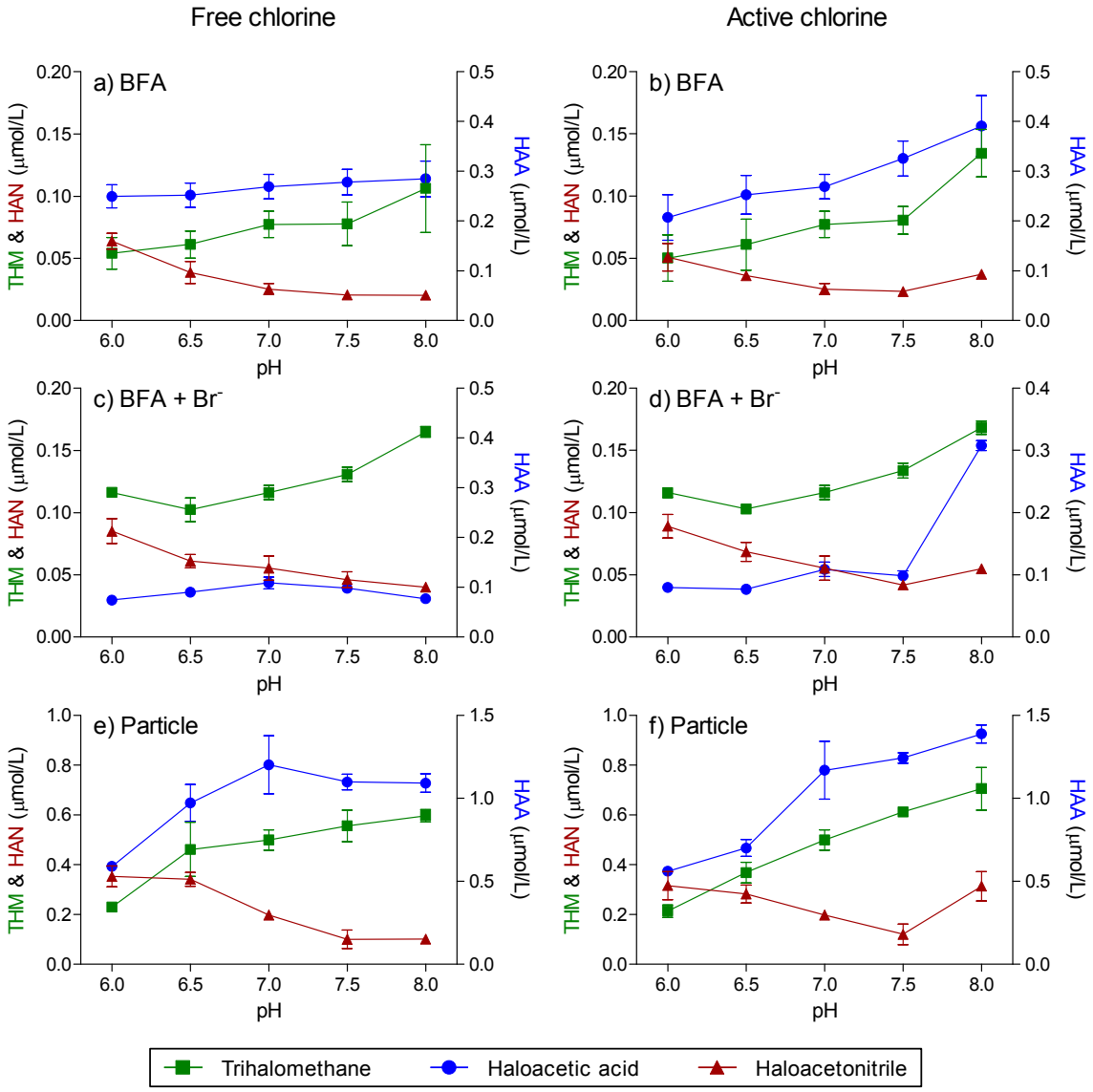

Figure 9. Effect of pH on formation of trihalomethanes (THMs), haloacetonitriles (HANs) and haloacetic acids (HAAs) during chlorination of body fluid analogue (BFA) (a-d) and particles (e and f). Chlorine was added as either constant free chlorine or constant active chlorine. Experimental conditions: body fluid analogue addition = 1 mg TOC/L, particle addition = 125 µg DOC/L, temperature = 25 °C, reaction time = 48 hours. Data from **Paper I** and **Paper II**.

Studies on drinking water chlorination have reported increased DBP levels in the presence of bromide (Chang et al., 2001; Hua et al., 2006; Hua and Reckhow, 2008). During chlorination of body fluid analogue the formation of THMs and HANs (Figure 9a and c) increased in presence of bromide whereas HAA formation decreased which may be due to the higher degree brominated HAAs (bromodichloroacetic acid, dibromochloroacetic acid and tribromoacetic acid)

were not analysed. The overall effect of pH on DBP formation was not affected by the presence of bromide while especially the formation of the different species of THMs was affected by the change in pH (**Figure 10**).

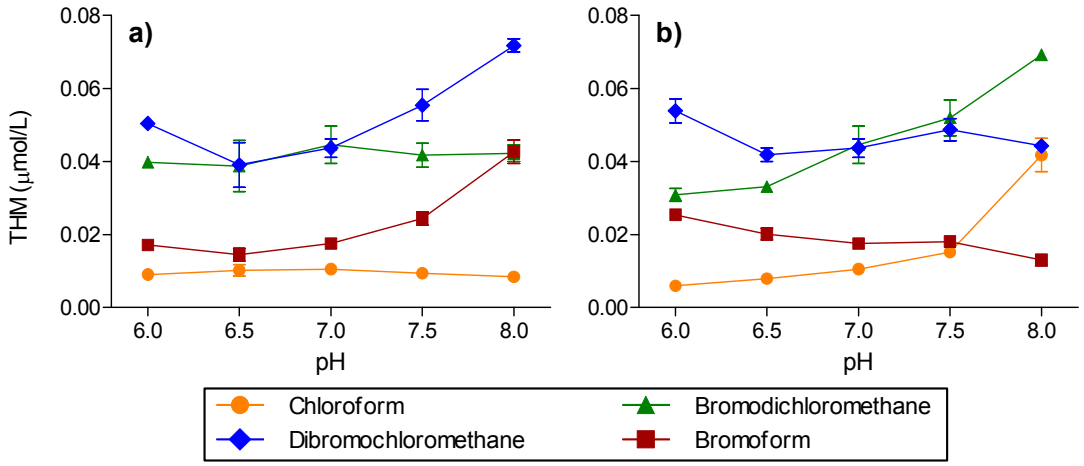

Figure 10. Effect of pH on the formation of different species of THMs during chlorination of body fluid analogue (BFA) at a) initial constant active chlorine and b) initial constant active chlorine. Experimental conditions: body fluid analogue addition = 1 mg TOC/L, bromide addition = 1 mg/L, temperature = 25 °C, reaction time = 48 hours. Modified from **Paper I**.

4.3.3 The effect of pH on trichloramine formation

The trichloramine formation from chlorination of body fluid analogue was investigated in **Paper I** and found to depend strongly of pH (Figure 11). The highest concentration was detected at pH 6.0 and it decreased continuously with increasing pH values. This pH dependency was confirmed by other studies, since trichloramine is one of the few DBPs where the pH dependency on its formation in pool water was previously investigated (Palin, 1950; Schmalz et al., 2011b). The trichloramine formation from particles was initially tested at pH 6.0 only and the formation was found negligible around the limit of quantification for the method (0.8 µmol/L (96 µg/L) (**Paper II**). This fits well with the results in a recent published paper (Schmalz et al., 2011b) where urea was found to be the main precursor for trichloramine during an investigation of different amides, amino acids, and amines. Urea is soluble and will not be caught in the filters. Hair and skin cells mainly consist of the three amino acids cysteine (17.5%), serine (11.7%) and glutamic acid (11.1%) (McElwee, 2011). Schmalz et al. (2011b) found that by reaction with chlorine 95% of urea was transformed to trichloramine at pH 5.9 but only 19% of glutamic acid and 15% of serine was found as trichloramine. Cysteine was not investigated, however, like alanine, it is

substituent at the alpha-carbon contrary to glycine and cysteine so it is expected to form very little trichloramine like alanine (5.4% at pH 5.9).

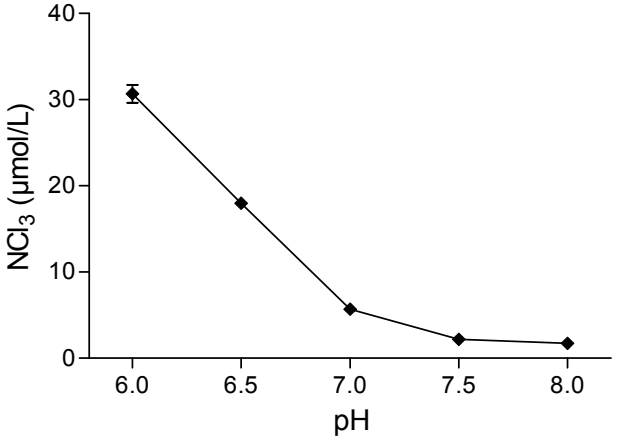

Figure 11. Formation of trichloramine from body fluid analogue. Experimental conditions: Body fluid analogue addition = 1 mg TOC/L, initial chlorine concentration = 35 mg/L, temperature = 25 °C, reaction time = 48 hours. Graph from **Paper I**.

4.3.4 The effect of pH on toxicity from organic DBPs

Since the formation of THMs, HANs and HAAs was affected differently by pH, the pH effect was evaluated by estimating the genotoxicity of the solutions based on the measured DBPs as described in **Paper I** and **Paper II**. The estimation is based on that the genotoxicity effect is additive. It was found that only the HANs contributed to genotoxicity unless bromide was present then the brominated HAAs contributed as well (Figure 12 and **Paper I**). Thus the highest genotoxicity was found at pH 6.0 with decreasing toxicity with increasing pH-levels. For body fluid analogue (Figure 12a) the genotoxicity was approximately the same level for pH 7.0 – 8.0 and an increase was seen at pH 6.5. While for the particles the platform was at pH 7.5 and 8.0 and an increase was already found at 7.0. When the bromide was added to the BFA solution the genotoxicity increased due to that the brominated DBPs are more toxic that their chlorinated analogue (Muellner et al., 2007; Plewa et al., 2002; Plewa et al., 2008). Furthermore, the toxicity had more a gradual increase with decreasing pH than the chlorination of body fluid analogue without bromide.

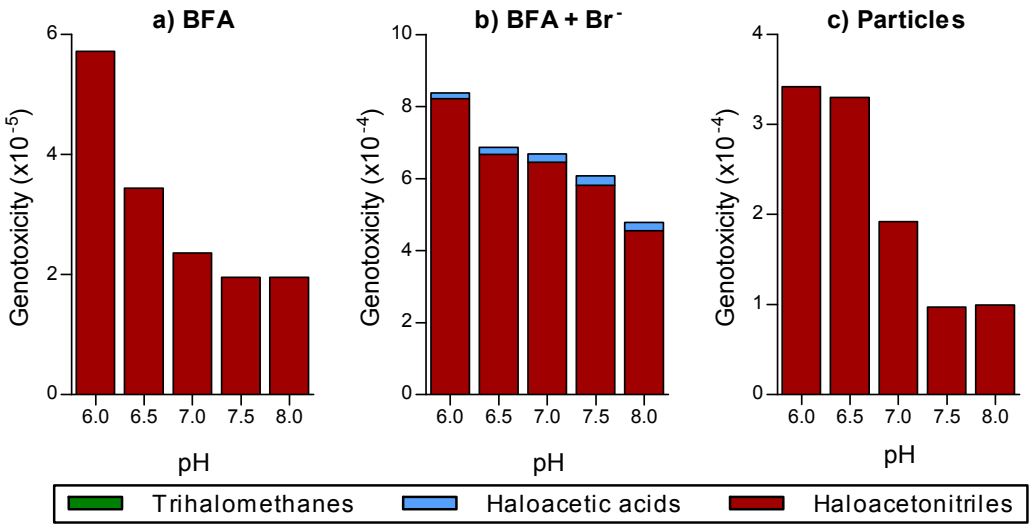

Figure 12. Estimated genotoxicity of chlorinated body fluid analogue (BFA) and particle solutions with constant initial concentration of free chlorine at $6.0 \leq pH \leq 8.0$. Data from **Paper I** and **Paper II**.

4.3.5 Optimal pH in swimming pools

To identify the lower limit of pH in swimming pools, the study with body fluid analogue was repeated with smaller pH intervals (**Paper IV**). The pH effect on the formation was as expected from the previous study (**Paper I**). The formation of chloroform is increasing with increasing pH whereas the dichloroacetonitrile is increasing with decreasing pH (Figure 13). However, the formation of dichloroacetonitrile was almost stable within pH 6.8 – 7.2, while at pH 6.7 and lower the formation increased considerably. The concentration of trichloroacetonitrile was close to the limit of quantification for the analysis and no conclusion on pH effect can be drawn. The trichloramine formation increased for $pH < 7.2$.

From the estimated genotoxicity it was found that the toxicity was approximately the same level in the pH range 6.8 – 7.5 and that it increased when pH was ≤ 6.7.

In general from analysed DBPs and the chosen experimental conditions, an optimal pH range for swimming pools with minimal DBP formation is identified at pH 7.0 – 7.2. In the wider pH range (pH 6.8 – 7.5) the effect on DBP formation was minimal compared to other factors which may affect the formation of DBPs in swimming pools. pH 6.8 should be an absolute minimum since both formation of HANs and trichloramine was found to increase significantly for pH below 6.8.

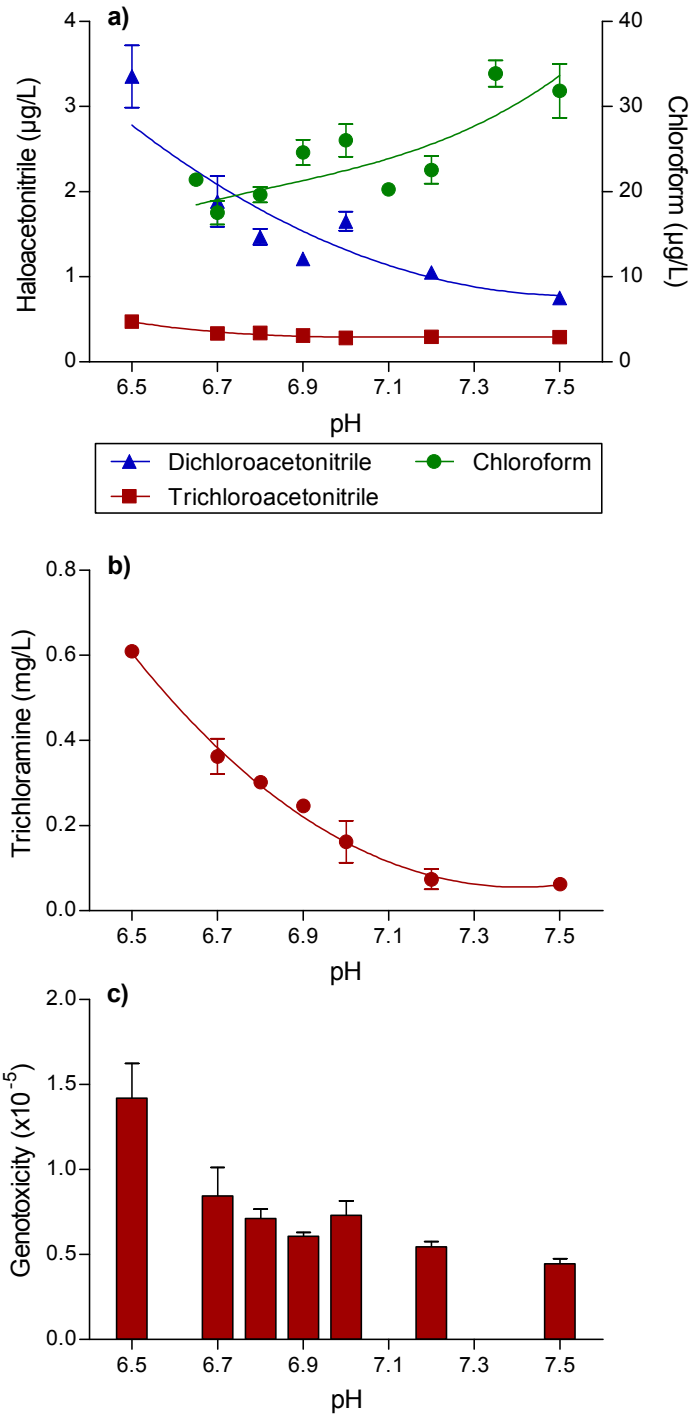

Figure 13. Formation of a) chloroform, dichloroacetonitrile and trichloroacetonitrile and b) trichloramine from body fluid analogue and c) estimated genotoxicity of chlorinated body fluid analogue solution. Experimental conditions: Body fluid analogue addition = 1 mg TOC/L, initial chlorine concentration = 35 mg/L, temperature = 28 °C. Modified from **Paper IV**.

5 Conclusions

This thesis provided an overview of strategies for coping with challenge of DBPs in swimming pools. The strategies were divided into the three groups: Alternatives to chlorination, removal of precursors and the formed DBPs, and inhibition of DBP formation.

None of the alternative disinfection agents which are used for private swimming pools met the requirements for disinfection agent for public swimming pools according to the Danish guideline and the German DIN. Thus chlorine is most likely as also the disinfectant in future public swimming pools.

The methods which were identified within the strategy of removing precursors and DBPs were pre-swim showering, filters, ozonation, activated carbon, air stripping, and UV treatment. Pre-swim showering and swimming hygiene is a key factor to ensure good pool water, since it would decrease the load of precursors. However, changing people's behaviour can be a difficult task. Filters are important to catch particles released by the bathers to ensure clear pool water. Furthermore, particles are precursors for different DBPs when reacting with chlorine. Thus, depending on the reaction time with chlorine needed to form DBPs fast removal of the particles could result in less formation of DBPs. Ozone is able to oxidise precursors so they get less reactive with chlorine. Furthermore, ozone is able to remove combined chlorine and other DBPs but the reaction is slow. Activated carbon is used for catalytic removal of combined chlorine and is able to adsorb both precursors and DBPs. However, if activated carbon is used in a column there is a risk of biological growth and that adsorbed precursors react with chlorine and form DBPs. Stripping is only able to remove volatile DBPs and is not changing the DBP formation potential of treated pool waters.

UV treatment is a good way to control combined chlorine. However, there is still a lack of knowledge about other processes occurring during UV treatment. UV treatment is able to remove many DBPs but with varying efficiencies. Chloroform and dichloropropanone were most difficult to remove while trichloronitromethane was easiest. In general, the efficiency increased with bromine substitution. Comparing applied UV dosage used for combined chlorine removal with degradation effectiveness suggests that significant removal of trichloronitromethane, chloral hydrate and the bromine containing haloacetonitriles and trihalomethanes occur as a beneficial side-effect of chloramine control by UV in swimming pools.

The last strategy was to inhibit the formation of DBPs. This may be achieved by reducing the chlorine concentration, temperature or pH level. However, in reality the possibility to change these parameters is limited in swimming pools due to comfort and safety of the bather. The pH level of the pool water can be operated within 6 – 8.0 without direct discomfort for the bathers. Within this range the formation of DBPs are affected differently. For both type of anthropogenic precursors (the soluble part and the particles) the formation of THMs decreased with decreasing pH while HAN formation increased. The effect of pH on the formation of HAAs depended on the precursor type. The particles did not form trichloramine during chlorination whereas the body fluid analogue formed trichloramine. The trichloramine formation showed strong pH dependency with increasing formation at pH below 7.0. The presence of bromide did not change the pH dependency on DBP formation, but it did increase the total amount of formed DBPs, except for HAAs. The estimation of the toxicity of the chlorinated samples allowed the comparison of THM decrease and HAN increase with decreasing pH. The toxicity increased with decreasing pH similar to the HAN formation. Furthermore, an optimal pH range for pool waters was identified to pH 7.0 – 7.2. In the wider pH range (pH 6.8 – 7.5) the effect on DBP formation was minimal compared to other factors which may affect the formation of DBPs in swimming pools.

A public swimming pool with water treatment optimised for low levels of DBPs should include several of the discussed methods since each method is specialised and has a main target e.g. UV treatment mainly removes combined chlorine and other easily photolysed DBPs while activated carbon and ozone remove precursors efficiently, particularly for THMs. The different methods used have to be optimised together to ensure the best water quality.

6 Perspectives

6.1 Significance of the work

The work has contributed to knowledge on formation of DBPs in swimming pools. More specific, it was during the experiments revealed that THMs cannot be used as a representative of all DBPs in swimming pools since the pH effect on the formation of THMs was opposite of the HANs. Thus THMs are not suitable for evaluation of technologies or change in operation such as pH-change.

Based on the results obtained in the PhD study and existing literature the pH range in the legislation for swimming pools in Denmark was changed from 7.0 – 8.0 to 6.8 – 7.6 with 6.8 being absolute minimum which should never be exceeded.

6.2 Suggestion for future research

The aim is to have microbiological safe swimming pool water with low level of DBPs especially the toxic ones. There is a lack of knowledge on achieving that. Research which could help getting there could be:

- Hydrolysis time of particle to gain knowledge on how often to back flush sand filter or need of faster removal such as drum filter and membrane filters.
- Treatment with ozone, and optimisation of contact time. Investigation of effects of pH on ozone treatment.
- Further investigation on UV treatment is needed to identify optimal range of UV irradiation where DBPs are removed and not formed.

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Papers

The following papers are included in the thesis:

I. Hansen, Kamilla M.S., Willach, Sarah, Antoniou, Maria G., Mosbæk, Hans, Albrechtsen, Hans-Jørgen and Andersen, Henrik R., 2012. Effect of pH on the formation of disinfection byproducts in swimming pool water – Is less THM better? *Water Research*, 46(19), 6399-6409.

II. Hansen, Kamilla M.S., Willach, Sarah, Mosbæk, Hans, Andersen, Henrik R., 2012. Particles in swimming pool filters – Does pH determine the DBP formation? *Chemosphere*, 87(3), 241-247.

III. Hansen, Kamilla M.S., Zortea, Raissa, Piketty, Aurelia, Vega, Sergio Rodriguez, Andersen, Henrik R., 2013. Photolytic removal of DBPs by medium pressure UV in swimming pool water. *Science of the Total Environment*, 443, 850-856.

IV. Hansen, Kamilla M.S., Albrectsen, Hans-Jørgen, Andersen, Henrik R., Optimal pH in chlorinated swimming pools – balancing formation of byproducts, Draft.

In this online version of the thesis, the articles are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from DTU Environment, Technical University of Denmark, Miljøvej, Building 113, 2800 Kgs. Lyngby, Denmark, reception@env.dtu.dk.

The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within four sections:
Water Resources Engineering, Urban Water Engineering,
Residual Resource Engineering and Environmental Chemistry & Microbiology.

The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

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